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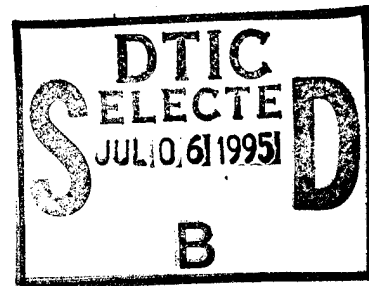
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Unimolecular and Bimolecular Exchange Reactions in Controlled Radical Polymerization

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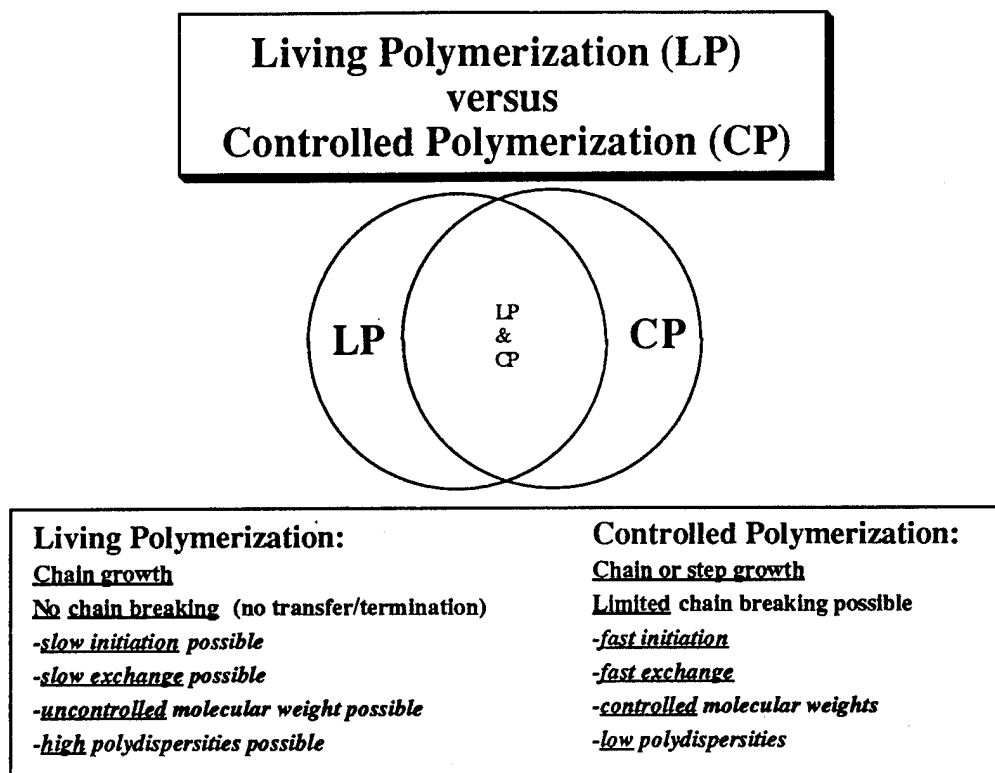4400 Fifth Avenue, Pittsburgh, PA 15213 USA

Introduction

Well defined polymers and block copolymers are usually prepared by living polymerizations in which there are no chain breaking reactions, transfer and termination. The absence of chain breaking reactions is, however, not a sufficient requirement for the synthesis of well defined macromolecules. Additionally, both initiation and exchange between species of various reactivities should be fast in comparison with propagation. Indeed, well defined polymers can be prepared even with systems in which chain breaking reactions do occur but their contribution is limited.[1] Systems in which transfer and termination can be quantitatively determined are only apparently living but they can provide well defined polymers, especially when relatively low molecular weight polymers are targeted.

Scheme 1 summarizes differences between living and controlled polymerizations. The former is essentially a chain growth process without chain breaking reactions but in which slow initiation and slow exchange between growing species of various activities are allowed. Slow initiation leads to polymerization degrees higher than the ratio of the concentration of the reacted monomer to that of the introduced initiator. This also results in polydispersities up to $M_w/M_n \approx 1.35$. Slow exchange may lead to much higher polydispersities and even to polymodal molecular weight distribution.

On the other hand, controlled polymerization is a synthetic method providing polymers with predetermined degrees of polymerization, $DP=\Delta[M]/[I]_0$, low polydispersities and potentially to end-functionalized polymers and copolymers. Controlled polymerization can either be a step-growth or a chain-growth process. It also allows some limited

contributions of chain breaking reactions. Simply, targeted molecular weights have to be tuned to values at which the proportion of chains marked by transfer and termination is relatively small, e.g. < 5%.

Scheme 1

**Living Polymerization (LP)
versus
Controlled Polymerization (CP)**

Living Polymerization:
Chain growth
No chain breaking (no transfer/termination)
-*slow initiation* possible
-*slow exchange* possible
-*uncontrolled molecular weight possible*
-*high polydispersities possible*

Controlled Polymerization:
Chain or step growth
Limited chain breaking possible
-*fast initiation*
-*fast exchange*
-*controlled molecular weights*
-*low polydispersities*

Termination in radical polymerization proceeds by growing radicals terminating in a bimolecular fashion, either by coupling or by disproportionation. Thus, radical polymerizations, in contrast to ionic polymerizations, can not be living, although, as will be demonstrated later, they can produce well defined polymers and copolymers, i.e. they can be controlled.

Effect of Slow Initiation, Termination, and Transfer on Kinetics, Molecular Weights and Polydispersities.

The number of growing species and the number of chains should be constant in living polymerizations, provided that initiation is fast in comparison with propagation. If the polymerization is first order in monomer, then a constant number of growing species should lead to straight, semilogarithmic, kinetic plots. However, as shown in Figure 1, a considerable deviation from linearity is found if initiation is slow or if termination occurs.
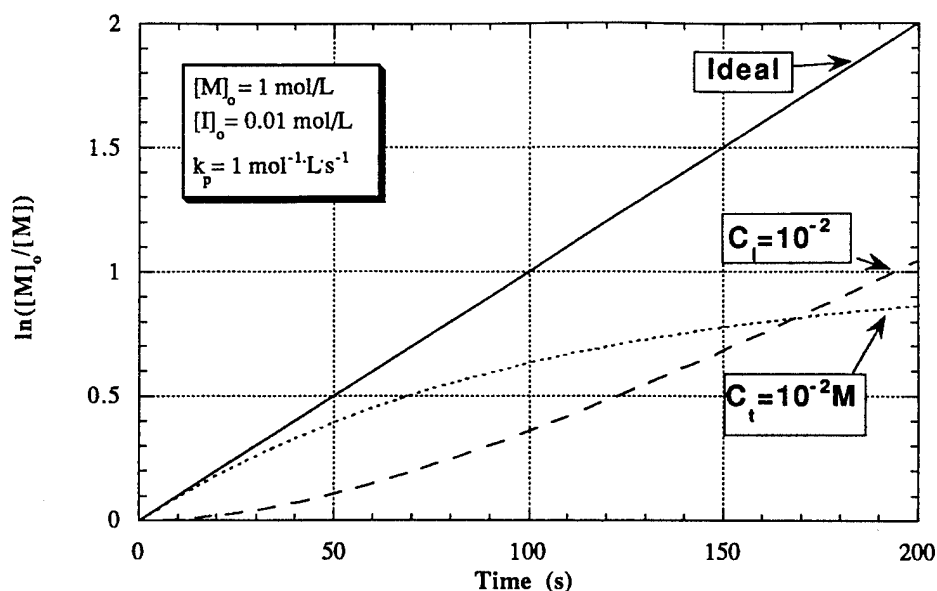
Fig. 1. Effect of slow initiation and termination on kinetics.

The magnitude of the deviation depends on the ratio of the rate constants of initiation to propagation, $C_i = k_i/k_p$, and termination to propagation, $C_t = k_t/k_p$, for slow initiation and termination, respectively. In the case of slow initiation, polymerization continuously accelerates and polydispersities decrease with conversion and may reach values close to those for the ideal living system. On the other hand, termination leads to progressive rate reduction and to an increase in polydispersities. Depending on the magnitude of k_t/k_p and the ratio of $[M]_0/[I]_0$, conversions may reach a limiting value. Polydispersities increase as the reaction progresses and in the particular case of unimolecular termination with $C_t = 10^{-2}$ M and $[M]_0/[I]_0 = 10^2$, conversion is limited to 63%, resulting in a polymer with $DP_n = 63$, instead of $DP_n = 100$. The final polymer also has a considerably higher polydispersity, $M_w/M_n = 1.4$, than for an ideal, living polymer, $M_w/M_n < 1.1$. Transfer reactions, should have no effect on kinetics, providing that regeneration of active sites is fast, but transfer has a pronounced affect on molecular weights and polydispersities. It has to be noted that straight kinetic plots can also be obtained under steady - state conditions when the number of growing species is constant because the rate of initiation is equal to that of termination. However, in that case molecular weights do not increase with conversion, as discussed below.

If the number of chains is equal to the number of initiator molecules and initiation is fast, then in the absence of transfer, the degree of polymerization increases linearly with

conversion according to the formula $DP = \Delta[M]/[I]_0$. Unimolecular termination by disproportionation in radical systems should have no effect on molecular weights, and they should still increase linearly with conversion, although limited values of DP are possible. On the other hand, both slow initiation and transfer have significant effects on evolution of molecular weights with conversion, as shown in Figure 2.
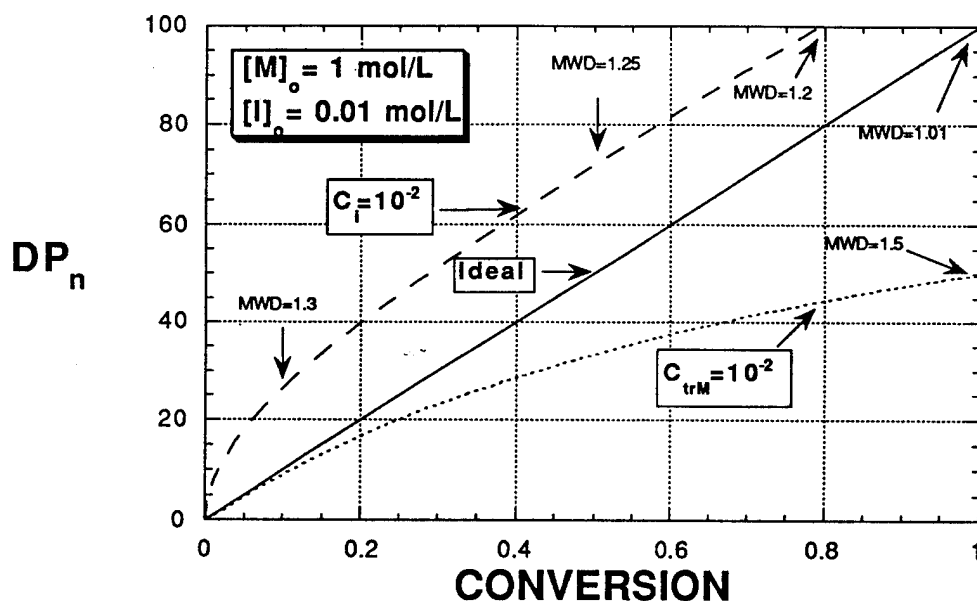

Fig. 2 Effect of slow initiation and transfer to monomer on evolution of molecular weights with conversion

For slow initiation, the molecular weights tend to be initially higher than predicted and as the reaction progresses, they asymptotically reach values for ideal living system. If initiation is very slow, like in most classic radical processes, very high molecular weights, $M_n > 100,000$, are formed at very low conversions ($< 1\%$) and subsequently, molecular weights may even decrease with conversion. Molecular weights do not increase linearly with conversion if the contribution of transfer is significant. For example, in the case of transfer to monomer, if $C_{tr} = k_{trM}/k_p = 10^{-3}$ and $[M]_0/[I]_0 = 10^3$, then instead of $DP_n = 1000$, the value of $DP_n = 500$ will be obtained and the polydispersity will be $M_w/M_n = 1.5$. However, if the transfer coefficient is the same, but a smaller ratio $[M]_0/[I]_0 = 10^2$ is used, then the deviation from the ideal behavior becomes much smaller and a polymer with $DP_n = 85$, instead of $DP_n = 100$ is formed. Polydispersities are also considerably reduced to $M_w/M_n = 1.15$. Thus, the proportion of chain breaking reactions depends strongly on the targeted molecular weights

and for sufficiently low molecular weights, well controlled polymers can be prepared, even in the presence of chain breaking reactions. This principle is widely used in new "living" systems, for example in the carbocationic [2], group transfer [3] and sometimes in organometallic systems.

Figure 3 shows the dependence of the ratio of chains which have been irreversibly deactivated by either termination or transfer, to monomer, counter ion or transfer agent, to the total number of chains. If this ratio equals zero, all chains are active and potentially functionalizable; if the ratio equals 1, then all chains are deactivated.
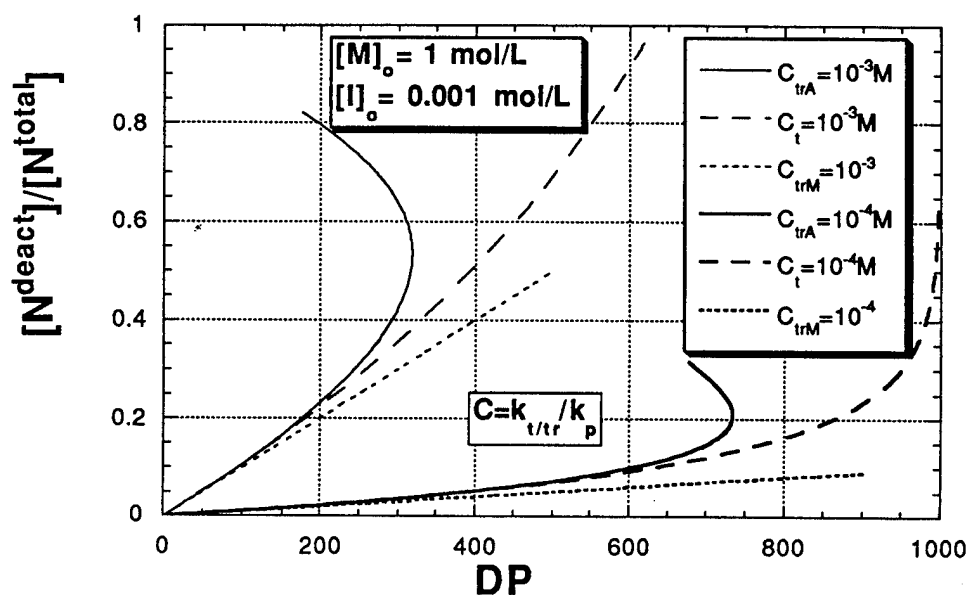

Fig. 3 Effect of degree of polymerization on the proportion of chains deactivated by chain breaking reactions.

As shown in Figure 3, the proportion of deactivated chains increases with chain length and also with the ratio $k_{t/tr}/k_p$. The proportion of deactivated chains can be significantly reduced for the same transfer/termination coefficient, if low molecular weight polymers are synthesized.

In the case of transfer to monomer, the proportion of deactivated chains increases monotonously with conversion up to a certain value at the final conversion. For transfer to transfer agent or to counterion, by either a unimolecular or pseudounimolecular process, the proportion of deactivated chains continuously increases and the average molecular weight decreases at high conversions because the rate of transfer is constant but the rate of

propagation decreases at low monomer concentration. For the case of termination, it is necessary to stop the reaction at an appropriate stage; otherwise all chains will become deactivated.

Concept of Controlled Radical Polymerization.

As discussed in the previous section, controlled polymerization requires a low proportion of deactivated chains, which can be achieved by keeping polymer molecular weights sufficiently low. This requires a relatively high concentration of the initiator or, in other words, low $[M]_0/[I]_0$ ratios. However, at high $[I]_0$, a large concentration of radicals, $[P*]$, is expected and, because in radical process termination is bimolecular, the contribution of termination would become more significant.

In order to solve the discrepancy between high $[I]_0$ and low $[P*]$, it is necessary to establish an exchange between dormant and active species. The concentration of the dormant species can be equal to $[I]_0$ and the concentration of momentarily growing species to $[P*]$. The total number of growing chains will be equal to $[I]_0$ ($\approx [I]_0 + [P*]$), and radicals would be present at a very low stationary concentration, $[P*]$, and therefore the contribution of termination and the proportion of irreversibly terminated chains should be very low. There are three possible scenarios to realize the concept of controlled radical polymerization.[4]

1. Degenerative transfer:

$$P_n{}^\bullet + P_1\text{-}R \xrightleftharpoons{k_{tr}} P_1{}^\bullet + P_n\text{-}R$$
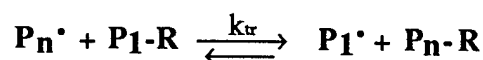
The idea of degenerative transfer is based on a thermodynamically neutral exchange reaction between active and dormant species. This can be visualized as transfer of the R moiety between all chains in such a way that the concentration of P* remains very low and number of chains roughly corresponds to [P-R]. P-R can not react directly with monomer and P-R can not react with one another; it can react only with P*. P* would be generated by a classic radical initiating system such as AIBN, BPO, redox, etc. P* can react with monomer, for propagation, with P-R, for degenerative transfer, and can also react one with another, for termination. The latter reaction can not be completely avoided, although its contribution will depend on the concentration of P*, as described previously. Nevertheless, the maximum amount of deactivated chains would be equal to that of the introduced initiator, $[I]_0$. If the concentration of the transfer agent is much higher than that of the initiator, $[P\text{-}R]_0 \gg [I]_0$, then the proportion of deactivated chains will be low enough and controlled polymerization can be accomplished. This additionally requires fast exchange between

growing radicals, P*, and the dormant species, P-R. It is worth noting that fast initiation is not required in this case. There are only a few examples of such reactions, and one of them, based on alkyl iodides, will be discussed later.

2. Reversible homolytic cleavage of covalent species:

$$P\text{-}R \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P^{\bullet} + R^{\bullet}$$
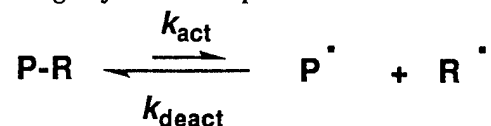
The covalent species P-R can reversibly and homolytically cleave to produce the growing radical P*, capable of propagation, and the dormant radical R*, which, ideally, should react only with P* but not with the monomer or with itself to form inactive dimers. P* can react not only with M and R* but also with another P*, leading to termination. Because termination rate is proportional to $[P*]^2$, and propagation rate to $[P*]$, the contribution of termination and the proportion of deactivated chains increases with $[P*]$.

This case is probably most frequently represented in the search for controlled radical polymerizations. As examples of R*, dithiocarbamate radicals,[5, 6] nitroxyl radicals,[7, 8, 9, 10] and also bulky organic radicals such as triphenylmethyl and substituted diphenylmethyl species can be used [11, 12]. The problems with most of them, except nitroxyl radicals, is that the scavenging radicals can initiate the polymerization themselves and that they participate in side reactions leading to the degradative, not degenerative, transfer. Some systems involving nitroxyl radicals will be discussed in detail later.

3. Reversible homolytic cleavage of persistent radicals:

$$P^{\bullet} + X \underset{\longleftarrow}{\longrightarrow} \{P\text{-}X\}^{\bullet}$$
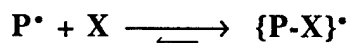
The persistent radical {P-R}* should only cleave homolytically to form P* and the species R, but it should not react with monomer. R should be an inert compound capable only of reacting with P*. P*, as in the previous cases, is a typical growing radical which can react with R*, with M, and with P*. As before, if $[P*]$ is very low, the proportion of deactivated chains is low as well.

The role of R can be played by some elementoorganic or organometallic species with an even number of electrons. Some success has been reported with group XIII and XV elements such as aluminum [13] and phosphorus [14] as well as with organometallic derivatives of Co,[15, 16] Cr,[17, 18, 19] and other transition metals. It should be stressed

that in some cases not only radical but also ionic and / or coordinative polymerization may occur, and it is necessary to carefully evaluate the mechanism of the polymerization. In some systems, it may happen that both mechanisms can operate simultaneously. That is, not only homolytic but also heterolytic bond cleavage may take place. The proportion of each pathway will depend on the nature of the metal or element, ligands and medium effects.

4. Mixed systems

Degenerative transfer may operate simultaneously with systems based on the reversible cleavage of covalent species and persistent radicals. This essentially means that in addition to unimolecular exchange, the bimolecular process based on the degenerative transfer may take place. For example, the use of alkoxyamines together with classic radical initiators pose the possibility of both reactions 1 and 2.

Degenerative Transfer

The basic requirement for degenerative transfer is the sufficient thermal stability of P-R and fast exchange with P* in comparison with propagation. This means that the transfer coefficients should be similar to or larger than 1. This is necessary for the preparation of well defined polymers, especially when $[M]_0 \gg [P\text{-}R]_0$. Additionally, the reactivity of the P_1-R species in the initially added transfer agent should be similar to or higher than that in the macromolecular species P_n-R. Thus, P_1* should be similar to the growing radical P_n*. Inspection of transfer coefficients indicates that large k_{tr} / k_p values are found for compounds with very labile E-Z bonds such as S-S, Si-H, P-H or Br₃C-Br. As mentioned before, the degenerative nature of the process requires that P* must be a carbon centered species, i. e., a 1-phenylethyl derivative for styrene polymerization. Of course, the C-H bond is not sufficiently labile. Apparently, 1-phenylethyl sulfides are not reactive enough either. Thus, in addition to considering organometallic species, the corresponding alkyl iodides were examined by our group for use as the P-R species.[20]

Although the C-I bond can also be cleaved heterolytically, this does not happen for styrene derivatives below 100 °C. Spontaneous, homolytic cleavage does not happen either at reasonable rates for T < 100 °C, as proved in blank experiments. However, addition of 1 - phenylethyl iodide to the polymerization of styrene initiated by AIBN had a tremendous effect on the evolution of molecular weight with conversion and on polydispersities.

The polymerization of styrene was initiated by AIBN at two different concentrations, $[AIBN]_0 = 0.01$ mol / L and 0.03 mol / L, in the presence of two different concentrations of 1 - phenylethyl iodide, $[1 - PEI]_0 = 0.1$ mol / L and 0.3 mol / L. As shown in Figure 4, the

transfer agent had a slight effect on the kinetics of styrene polymerization at 70 °C. An increase in the amount of transfer agent slowed the rate of polymerization.
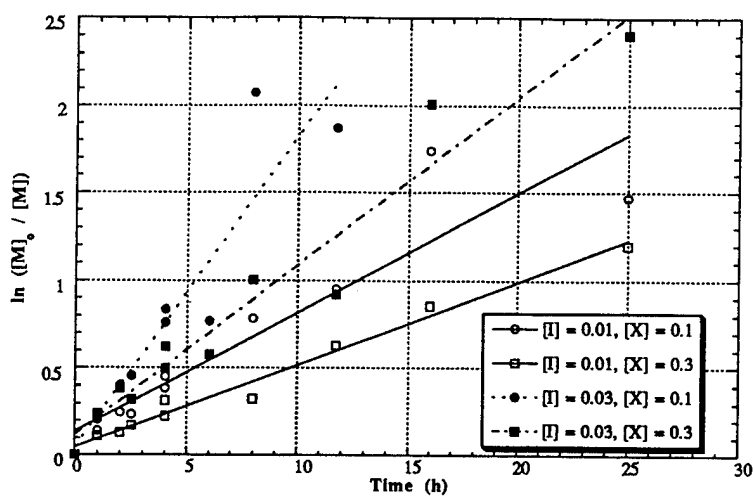

Fig. 4 Kinetics for the bulk polymerization of styrene at 70 °C, [I] = AIBN, [X] = 1 - phenylethyl iodide.

The molecular weights were dramatically affected by the presence of the degenerative transfer agent, as shown in Figure 5.
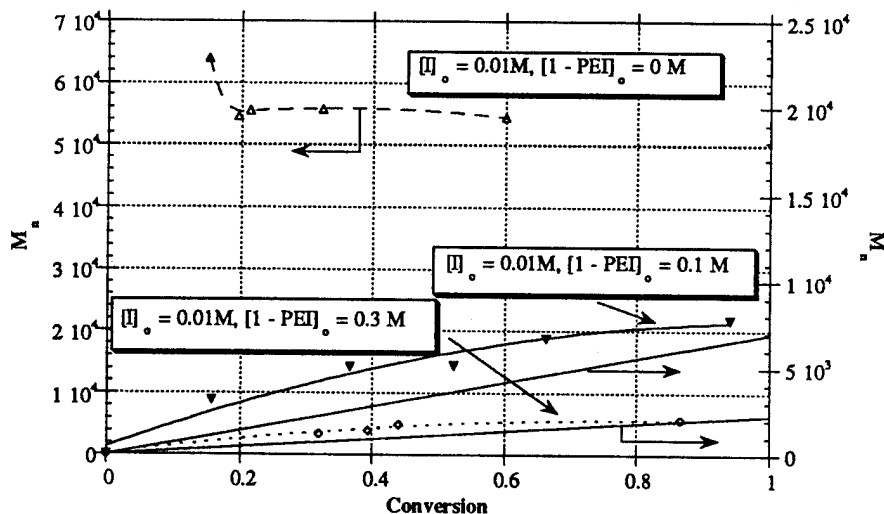

Fig. 5 Dependence of M_n upon conversion for the bulk polymerization of styrene at 70 °C, [I] = AIBN, [1-PEI] = 1 - phenylethyl iodide.

The degree of polymerization followed the simple relationship $DP_n = \Delta[M]/[1\text{-}PEI]_0$. DP_n values were initially higher than predicted by the ideal law, probably because of the limited value of the transfer coefficient and relatively slower exchange.

Dependence of polydispersities on conversion, shown in Figure 6, confirms relatively slow exchange.
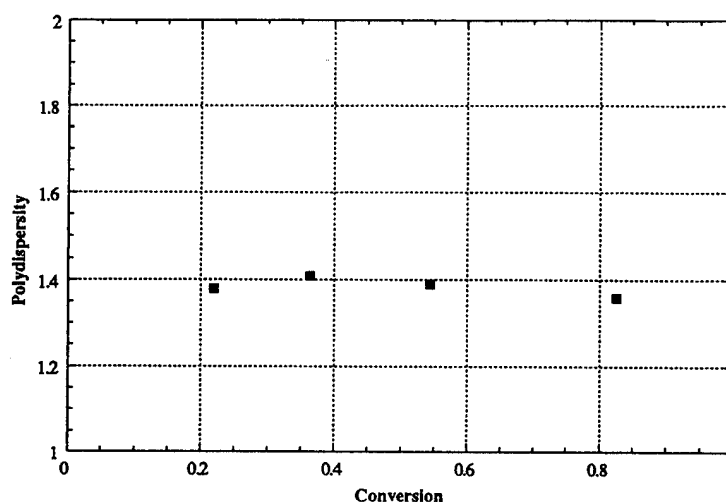

Fig. 6 Polydispersity versus conversion for the bulk polymerization of styrene at 70 °C, $[I]_0$ = 0.01 M, $[1\text{-}PEI]_0$ = 0.1 M.

Polydispersities essentially remained constant with conversion but were higher than predicted by the Poisson distribution, $M_w/M_n \approx 1 + 1 / DP_n$. Bulk polymerization in the presence of AIBN alone led to polydispersities $M_w/M_n > 2$.

Thus, the polymerization of styrene in the presence of degenerative transfer agents followed typical behavior of controlled polymerization such as low polydispersities and a linear evolution of molecular weight with conversion, although it was initiated by classic radical initiators. Moreover, addition of a new portion of monomer or addition af another monomer extends chain growth. In this way, block copolymers between polystyrene and poly(butyl acrylate) have been prepared.

Reversible Homolytic Cleavage of Alkoxyamines

Alkoxyamines have been successfully used in the preparation of well defined polymers by a radical mechanism. The lability of the C-ONR_2 bond depends very much on the substituents on the carbon atom. Polar substituents, such as those in the polymerization

of acrylics and vinyl acetate, as well as sterically crowded tertiary species, led to homolytic cleavage at temperatures below 100 °C. However, in the polymerization of styrene, temperatures above 120 °C were required in order to assure sufficient dynamics of the exchange process. At this temperature, styrene is polymerized radically by self-initiation without any radical initiators. The self - initiation proceeded via formation of the Diels - Alder dimers which produced radicals through the process of aromatization [21]. We have previously reported the use of TEMPO in the self - initiated polymerization of styrene in order to prepare well - defined polymers.[10, 22] Although, addition of TEMPO allows for the possibility of controlling molecular weights, polymers with relatively broad molecular weight distributions were formed. This was due to the continuous generation of radicals by self-initiation.

It has been reported that protonic acids reduce the rate of self-initiation and lead to more well defined systems.[9, 21] However, acids catalyze the formation of Diels - Alder adducts and may also lead to cationic polymerization and / or the formation of indan - type dimers. Thus, the best solution is to increase the lability of the C - ONR$_2$ bond in order to perform the polymerization at sufficiently low temperatures, when self initiation is impossible.

We have attempted several methods to increase the rate of homolytic cleavage and to shift the position of the equilibrium between active and dormant species without increasing the reaction temperature. The simplest method of checking the effect of additives or structural changes within the nitroxyl radical is to compare the overall rates of polymerization, which are proportional to the concentration of growing radicals and to analyze the evolution of molecular weight with conversion. If the total number of dormant species remains constant, the molecular weight should not be affected by the structural changes. In such a case, the rate increase can be solely assigned to a shift in the equilibrium towards growing radicals.

First, we have used different solvents and found that increasing solvent polarity from decaline, to bulk styrene, and to diglyme, had a very small effect on both the kinetics and molecular weights. Addition of H - bonding species such as alcohols had a stronger affect on rates. This could be explained by the H - bonding to alkoxyamine, facilitating homolytic cleavage. It was also possible that the nitroxyl radical may have become less reactive because of the H - bonding which would be facilitated by a partial negative charge on the oxygen atom in the nitroxyl radical. We followed this observation by using nitroxyl radicals with the attached phosphoric acid moiety. The rate of polymerization of styrene, as shown in Figure 7 increased significantly when TEMPO was substituted with 4-phosphonooxy-TEMPO.
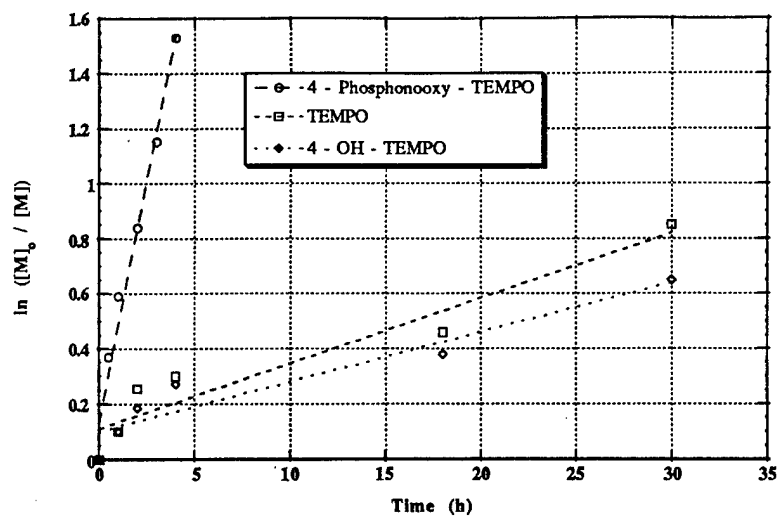
Fig. 7 Kinetics for the bulk polymerization of various TEMPO derivative at 120 °C.

At the same time, molecular weights did not change substantially, indicating a similar number of chains in the dormant state, Figure 8.
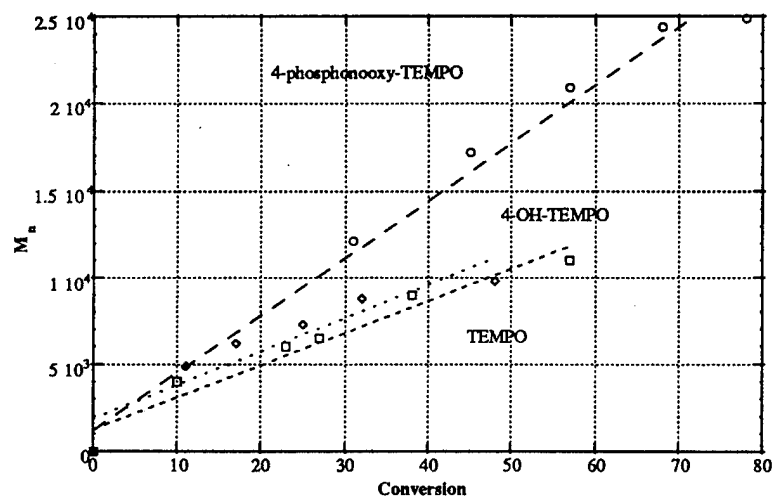

Fig. 8 Dependence of M_n upon conversion for the bulk polymerization of styrene with various TEMPO derivative at 120 °C.

4 - Hydroxy TEMPO does not act in a similar way, probably because both N - O* and - OH substituents are in equatorial positions and can not provide efficient H - bonding.

The potential explanation of the hydrogen bonding in both systems is shown schematically below.
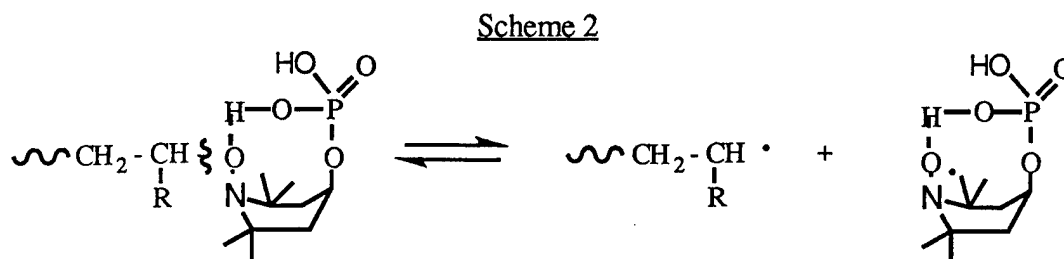
Another approach was based on the complexation of nitroxyl radicals with Lewis acids and with transition metal complexes. However, the rates of polymerization for styrene and MMA initiated by AIBN in the presence of 4 - phenyl - 2, 2, 5, 5 - tetramethyl - 3 - imidazolin - 1 - yloxy - 3 - oxide were only very weakly affected by the addition of transition metals such as manganese (II) hexafluoroacaetylacetonate. In fact, the rate of the MMA polymerization was accelerated two fold by the addition of an equimolar amount of the manganese salt, but the rate of the styrene polymerization was reduced in the presence of the manganese salts. Thus, this system has not been efficient for shifting the equilibrium between active species and dormant species towards the former.

Homolytic Cleavage of Persistent Radicals

Persistent radicals can reversibly and homolytically cleave to form species with an even number of electrons and reactive organic radicals. In order to assure a controlled radical polymerization, the equilibrium should be strongly shifted towards the dormant, persistent radicals. The released organic radical may react with monomer and return to the dormant state after several propagation steps. The repetition of this process will provide continuous growth of all chains and well defined polymers. We have previously reported the polymerization of vinyl acetate using organoaluminum persistent radicals stabilized by bidentate aromatic amines and activated by stable radicals such as nitroxyl radicals [13]. This system is, however, very sensitive to moisture and oxygen, and small amounts of moisture / oxygen apparently activate the system, but larger amounts appear to deactivate it.

Another organometallic system is based on chromium derivatives.[17] Here, ligands around the metal center play a very important role. The same is true for cobalt derivatives. As recently reported, transfer observed for the cobaloxime / MMA system is strongly reduced in the polymerization of acrylates.[15, 16] The polymerization of ethyl acrylate initiated by isopropyl pyridinato cobaloxime led to well defined systems in which molecular weight grew slowly but linearly with conversion providing well defined polymers.[16]

It must be stressed that polymerization with organometallic compounds may proceed not only by a radical but also by an ionic or a coordinative mechanism. In fact, there is a number of very similar initiation systems which have been ascribed to anionic / coordinative polymerization[23]. It is necessary to use various scavengers, to study solvent effects, and copolymerization relationships in order to elucidate the mechanism in an unambiguous way.

Conclusions

Well defined polymers can be produced by radical polymerization using three different approaches: degenerative transfer, reversible homolytic cleavage of covalent species, and reversible homolytic cleavage of persistent radicals. The first method requires high degenerative transfer coefficients but allows for slow initiation, the other two methods require that the equilibrium be strongly shifted towards dormant species, and that initiation is fast. All three approaches may provide controlled polymerizations, but not living polymerizations, because chain breaking reactions can not be eliminated although their contribution can be strongly reduced.

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